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Extraction of iron from vanadium slag using pressure acid leaching

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Abstract

The extraction of iron from vanadium slag was attempted using pressure acid leaching. The effects of the several parameters which included reaction time, H^+/slag ratio, leaching temperature, and concentration of additive (Na_2S) upon leaching efficiency of iron were investigated. The results showed that the leaching efficiency of iron could reach above 76% in the best leaching condition. By using Leaching solution as iron source, Fe_2O_3 hollow spheres have been successfully synthesized via facile hydrothermal method by using carbon spheres as template followed by a subsequent heat treatment. The experimental results show that hollow spheres structures of Fe_2O_3 with the mean particle size of 0.9-1.2 μm is single hexagonal crystal system.

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Keywords: iron; vanadium slag; pressure acid leaching; hollow spheres

1. Introduction

Vanadium is an important product that is used almost exclusively in ferrous and non-ferrous alloys due to its physical properties such as high tensile strength, hardness, and fatigue resistance[1]. In China, vanadium resource is

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abundant in vanadium-titanium magnetite ores, from which vanadium-containing hot metal is obtained in blast furnace[2,3]. The recovery methods of vanadium from vanadium slag have recently been discussed. The well-known methods of roasting leaching process is introduced to recover vanadium from vanadium slag. The roasting process is that the preparation of mixtures of slag with a sodium salt which can be one or combination of NaCl, Na_2CO_3 and Na_2SO_4 under an oxidizing atmosphere, which will convert the vanadium oxide of vanadium slag into water soluble sodium vanadate[4]. In other cases, calcium salt is also used in the roasting stage, and calcium vanadate formed in roasting can be dissolved by leaching with acid or alkali[5,6].

In the recovery methods of vanadium from vanadium slag, iron from slag is not involved in the reaction, which is used as a waste residue. The vanadium slag which contains 30%-40% Fe_2O_3 has high recovery value. The main methods of extraction iron have been made during the last decades for possible alternative extraction iron from the slag as such in different domains like magnetizing roast, flotation iron, blending iron etc.

In this work, the high pressure acid leaching is adopted to extract iron from vanadium slag. The effects of various parameters including reaction time, H^+/slag ratio, leaching temperature, and concentration of additive (Na_2S) are explored. Then, the Fe_2O_3 with hollow spherical morphology is synthesized by using vanadium slag as iron source. The morphologies and structures of precursor and as-prepared phosphors were characterized by XRD, IR and SEM.

2. Material and methods

2.1 Materials

The vanadium slag used in the study was provided from Chengde special steel Co., Ltd., Heibei Province, China. The slag was ground using a planetary high-efficient ball mill and its chemical composition was analyzed by XRF. The results were presented in Table 1. An XRD of the vanadium slag was presented in Fig. 2. It showed that the slag contains MgV_2O_4, Fe_2SiO_4, Fe_3O_4 and $MnFe_2O_4$. All the reagents used were of analytical grade purity (Chinese medicine group) and were used without further purification.

Table 1. Chemical analysis of the vanadium slag

Component	V_2O_5	SiO_2	MnO	Cr_2O_3	CaO	TiO_2	Al_2O_3	TFe
wt.%	13.35	18.31	7.20	1.72	2.44	6.8	2.77	28.45

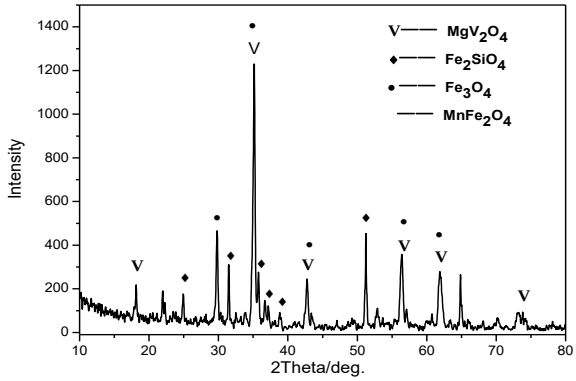

Fig. 1 XRD pattern of original vanadium slag sample

2.2. Experimental procedure

2.2.1 Iron leaching

A sample of 200 g dried slag was added to a titanium autoclave with an agitation of 500 rpm at the desired temperature and then oxygen was continuously aerated into the reactor to produce a total pressure of 1.2 MPa. The reaction time (after achieving the desired temperature), H^+/slag ratio, leaching temperature and additive (Na_2S)

concentration were varied. After the reaction was completed, the cover of autoclave was removed. The ore slurry was separated by vacuum filtration and the residue was analyzed for iron content.

2.2.2 Preparation of $FeSO_4 \cdot 7H_2O$

The acid leaching solution was reduced using Fe as the reduction agent at 50℃ for 3h, and then the solution was separated by vacuum filtration. $FeSO_4 \cdot 7H_2O$ was prepared by cooling crystallization using the filtered ferrous sulfate solution. The $FeSO_4 \cdot 7H_2O$ precursors were isolated by centrifugation at 5000 rpm. Next, the mixtures were dried at 100 ℃ for more than 3 h.

2.2.3 Synthesis of Fe_2O_3

A mixture of glucose monohydrate (40 mmol), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, 8 mmol), and 60 mL distilled water were heated at 180 ℃ for 15 h in a 100 mL Teflon-lined stainless steel autoclave under autogenous pressure. Then it was cooled to room temperature. The resulting precursors were isolated by centrifugation at 5000 rpm. Next, the mixtures were dried at 80 ℃ for more than 4 h. In a second step, Fe_2O_3 were obtained by heating the precursor in air at 600℃ for 3h and 1000 ℃ for 2 h, respectively.

2.2.4 Analysis of structure and morphology

Phase characterization of the prepared cathode materials was determined by X-ray diffraction (XRD) analysis using a Rigaku D/max-RB X-ray diffraction (Japan) with Cu K-radiation. The particles morphologies of prepared cathode materials were characterized using Hitachi S-3400N Scanning Electron Microscopy (SEM) . The groups on the samples were studied by Bruker Tensor37 infrared absorption spectroscopy (FTIR).

3. Results and discussion

3.1 Pressure acid leaching

3.1.1 Effect of H^+/slag ratio

The effect of H^+/slag ratio (mol/kg) on the leaching efficiency of Fe was studied in the range from 5:1 to 45:1.

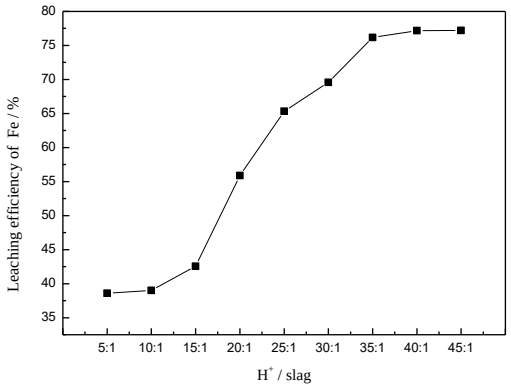

Fig. 2 The effect of H^+/slag ratio on the leaching efficiency of Fe

As shown in Fig. 2, the eaching efficiency of Fe extraction increased from 38.59% to 76.18% with an increase in H^+/slag ratio from 5:1 to 35:1. A further increase in H^+/slag ratio in the range from 35:1 to 45:1 did not noticeably affect the recovery of Fe. Although there was a little increase in the leaching efficiency of Fe when the H^+/slag ratio was above 35:1. There was also an increase in the residual concentration of H_2SO_4 in leachate. Therefore, if the residual H_2SO_4 from the leachate was not recovered using the diffusion dialyses method, a greater addition of ammonia would be required to adjust the pH, and this in turn would increase the production costs. Hence, an

H^+/slag ratio of 35:1 was chosen as being optimum.

3.1.2. Effect of reaction time

Fig. 3 reported the leaching efficiency of Fe obtained by varying reaction time from 10 to 180 min at 180 °C with H^+/slag ratio of 35:1 . An increase in the reaction time from 10 to 60 min led to a rapid increase in the leach recovery of Fe. However, the leaching efficiency of Fe did not increase significantly above 60 min reaction time. For subsequent reactions the time was kept to 60 min.

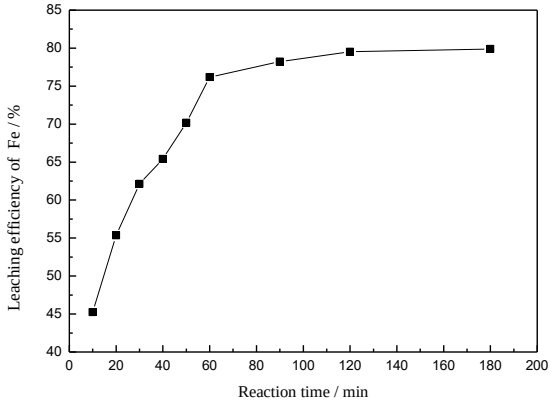

Fig. 3 The effect of reaction time on the leaching efficiency of Fe

3.1.3. Effect of leaching temperature

The effect of leaching temperature on the leaching efficiency of Fe with H^+/slag ratio of 35:1 and of 1.2ml/g for 60 min. The leaching efficiency of Fe versus leaching temperature was shown in Fig. 4.

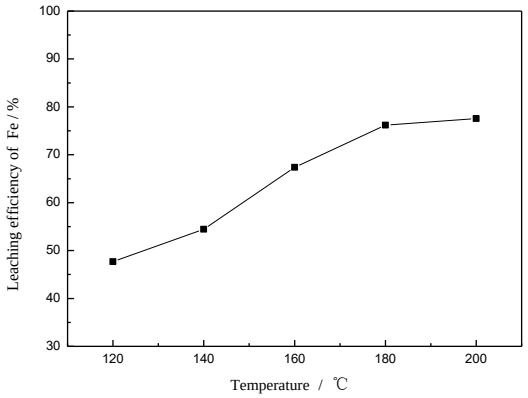

Fig. 4 The effect of leaching temperature on the leaching efficiency of Fe

Fe recovery increased obviously with an increase in temperature from 120 to 180 ℃, and a maximum of 76.18% of the Fe could be extracted. The leaching efficiency of Fe did not increase significantly above 180 ℃, for subsequent reactions the temperature was kept to 180 ℃. In atmospheric acid leaching process of extraction of Fe the leaching temperature was generally not higher than 95 °C. But, rising temperatures help improve the leaching

effiency and shorten the leaching time, this was a feature for the method of the Fe extraction used in this study.

3.1.4. Effect of additive (Na_2S) concentration

To increase the Fe leaching efficiency in the solution and further improve the kinetics of the reaction during leaching, the ability of S^{2-} to reduction was utilized to deoxidize the high valence Fe in this sample. For this reason Na_2S was chosen as an additive to the leaching process.

Fig. 5 reported the leaching efficiency of Fe obtained by varying additive concentration from 0 to 40.00 g/L. The Fe extraction increased only from 70.11% to 76.18% when the Na_2S concentration increased from 0 to 20.0 g/L. For further increases in the Na_2S concentration, the enhancement of Fe extraction was less pronounced, and the extraction increased from 76.18% at 20.0 g/L Na_2S to 77.34% at 60.0 g/L Na_2S. Overall, however, the additive concentration did not significantly affect the leaching efficiency of Fe.

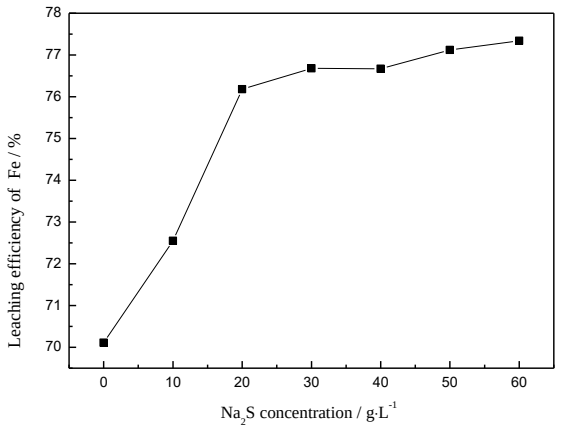

Fig. 5. The effect of additive (Na_2S) concentration on the leaching efficiency of Fe

According to results mentioned above, the optimum processing parameters for leaching procedure were a reaction time of 60min, H^+/slag ratio of 35:1, leaching temperature of 180 °C and additive (Na_2S) concentration of 20.0 g/L. Three parallel experiments were carried out using these optimum conditions. Results indicated a small variation in the leaching efficiency of Fe 76.20%, 76.15% and 76.29%. The average value was 76.2%.

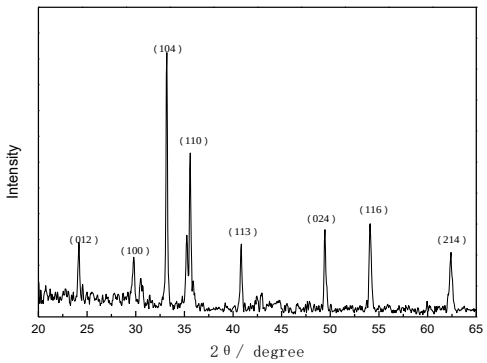

Fig. 6. XRD pattern of Fe_2O_3 by heating the precursor in air at 600℃ for 3h and 1000 ℃ for 2 h

3.2 Phase identification and transformation of the products

3.2.1 XRD characterization of Fe_2O_3

XRD pattern (Fig. 6) showed the sample were well-crystalline and exhibit diffraction peaks corresponding to (0 1 2), (1 0 0), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6) and (2 1 4) planes of hexagonal crystal system. The position and relative intensity of diffraction peaks are reasonably close to the standard data for hematite (JCPDS file No. 33-0664) which further indicates the purity of synthesized Fe_2O_3.

3.2.2 FTIR characterization of Fe_2O_3

The FTIR of the sample was shown in Fig. 7. The sample showed the main absorption in the regions 3427, 1612, 1032, 630, and 465 cm^{-1}. The general range of 3600–3100 cm^{-1} may be assigned to antisymmetrical and symmetrical O–H bonding stretching vibrational modes for water of hydration. The bonding in the region of 1670–1600 cm^{-1} also relates to O–H bonding bending vibrational modes. The bands at 465, 630 and 1132 cm^{-1} observed in sample can be attributed to metal oxygen stretching vibrational modes[7,8].

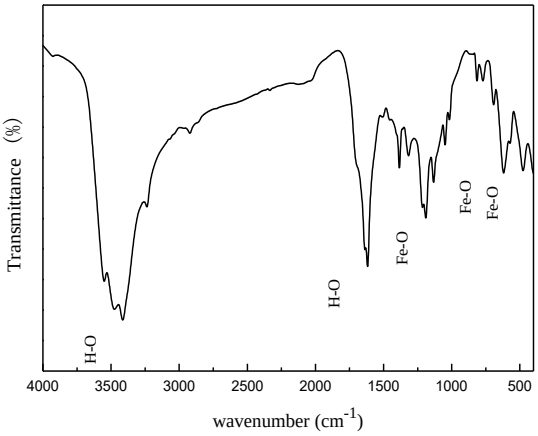

Fig. 7. Infrared (IR) spectrum of Fe_2O_3 by heating the precursor in air at 600℃ for 3h and 1000 ℃ for 2 h

3.2.3 SEM characterization of Fe_2O_3

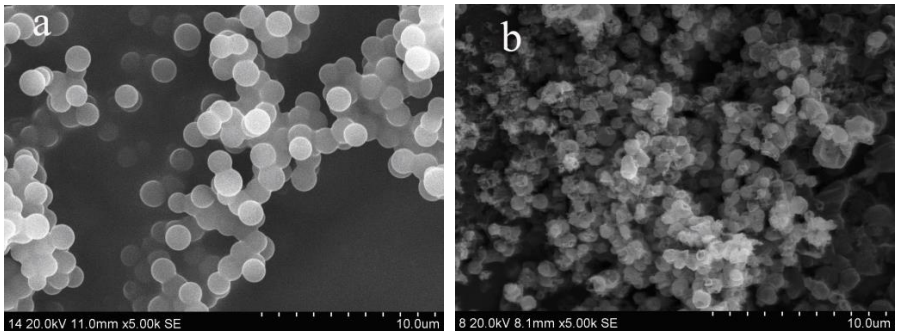

Fig. 8. SEM pattern of Fe_2O_3 (a): precursors, (b): heating the precursor at 600℃

Under the prescribed conditions, the samples showed favorable dispersivity as measured by SEM, as shown in Fig.

7. The SEM of precursors particles prepared by hydrothermal synthsis at 180 ℃ for 15 h indicated that the precursors samples consist of uniform separated spheres with diameter of about ca. 1.2-1.5 μm in Fig. 8(a) . The SEM of particles prepared by post annealing at 1000 ℃ for 3 h indicated that the as-prepared samples also consist of uniform separated spheres with diameter of about ca. 0.9-1.2 μm in Fig. 8(b) . Particle size was smaller than that of the precursor for the shrink and densification in the formation of the sample. The SEM micrographs revealed that the presence of metal ions have little influence on the morphology of the products (Fig. 8(a, b)).

4. Conclusions

The recovery of iron from vanadium slag was performed using a process, which consisted pressure acid leaching, preparation of $FeSO_4 \cdot 7H_2O$ and synthesis of Fe_2O_3. The results indicated that pressure acid leaching was an efficient method for the extraction of iron from slags. Using the optimum conditions, which included a reaction time of 60 min, H^+/slag ratio of 35:1, leaching temperature of 180 °C and additive concentration of 6.206 g/L, the leaching efficiency of vanadium was above 76%. The carbon spheres with $FeSO_4 \cdot 7H_2O$ embedded precursors generated from carbonification of glucose have been explored for the synthesis of Fe_2O_3. The hollow spheres of Fe_2O_3 synthesized at 600 ℃ for 3 h and 1000℃ for 2h was single hexagonal phase and the diameter of about ca. 0.9-1.2 μm.

Acknowledgments

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